

CLAIMS

5 1. A method for solid free-form fabrication of a three-dimensional object, comprising:

- a) applying a particulate blend in a layer, said particulate blend including calcium aluminate particulates and polymeric binder particulates;
- 10 b) dispensing an aqueous polyol-containing liquid vehicle onto a predetermined area of the particulate blend to form hydrated cement in the predetermined area;
- c) hardening the hydrated cement; and
- d) repeating steps a) through c) such that multiple layers of the cement are formed that are bound to one another, thereby forming the three
- 15 dimensional object.

 2. A method as in claim 1, wherein the aqueous polyol-containing liquid vehicle is dispensed onto the predetermined area of the particulate blend by ink-jetting.

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 3. A method as in claim 1, further comprising the step of removing a portion of the particulate blend that does not form the hydrated cement.

 4. A method as in claim 1, wherein the polymeric binder particulates are

25 selected from the group consisting of 75% to 100% hydrolyzed polyvinyl alcohol powder, polyacrylamide powder, poly(acrylic acid), poly(acrylamide-co-acrylic acid), poly(vinyl alcohol-co-ethylene), poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid), poly(vinyl pyrrolidone), poly(methylmethacrylate-co-methacrylic acid), soluble starch, methylcellulose, and combinations thereof.

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5. A method as in claim 1, wherein the polyol of the liquid vehicle is selected from the group consisting of glycerol, ethoxylated glycerol, and combinations thereof.

5 6. A method as in claim 1, wherein the polyol of the liquid vehicle is polyethylene glycol having a weight average molecular weight from 200 Mw to 2000 Mw.

7. A method as in claim 1, wherein the step of hardening is accelerated
10 by including a particulate lithium ion source in the particulate blend.

8. A method as in claim 1, wherein the step of hardening is accelerated by including a solvated lithium ion source in the liquid vehicle.

15 9. A method as in claim 1, wherein the liquid vehicle further includes a colorant.

10. A method as in claim 1, wherein the liquid vehicle further comprises a low molecular weight polymer having a weight average molecular weight from
20 200 Mw to 2000 Mw.

11. A method as in claim 1, wherein the calcium aluminate particulates have an average particulate size from 10 microns to 80 microns, and wherein the polymeric binder particulates have an average particulate size from 0.5
25 microns to 80 microns.

12. A system for solid free-form fabrication of three-dimensional objects, comprising:
a particulate blend of calcium aluminate particulates and polymeric binder
30 particulates; and
an aqueous polyol-containing liquid vehicle configured for hydrating the particulate blend to form a cement.

13. A system as in claim 12, wherein the aqueous polyol-containing liquid vehicle is ink-jettable.

5 14. A system as in claim 12, further comprising a particulate lithium ion source admixed with the particulate blend.

15 15. A system as in claim 12, wherein the particulate lithium ion source is a member selected from the group consisting of lithium citrate, lithium
10 carbonate, lithium formate, and combinations thereof.

16. A system as in claim 12, further comprising a solvated lithium ion source solvated in the liquid vehicle.

15 17. A system as in claim 16, wherein the solvated lithium ion source is selected from the group consisting of lithium hydroxide, lithium carbonate, lithium citrate, and combinations thereof.

20 18. A system as in claim 12, further comprising an ink-jet pen configured for ink-jetting the liquid vehicle onto the particulate blend.

25 19. A system as in claim 18, further comprising a substrate configured for carrying the particulate blend in a defined region, said defined region being configured with respect to the ink-jet pen such that the liquid vehicle, upon being ink-jetted from the ink-jet pen, contacts the particulate blend.

20. A system as in claim 12, configured for applying multiple layers of cement such that each layer is bound to at least one adjacent layer.

30 21. A system as in claim 12, wherein the polymeric binder particulates are selected from the group consisting of 75% to 100% hydrolyzed polyvinyl alcohol powder, polyacrylamide powder, poly(acrylic acid), poly(acrylamide-co-

acrylic acid), poly(vinyl alcohol-co-ethylene), poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid), poly(vinyl pyrrolidone), polymethylmethacrylate-co-methacrylic acid, soluble starch, methylcellulose, and combinations thereof.

5 22. A system as in claim 12, wherein the polymeric binder particulates have a weight average molecular weight from 2,000 Mw to 1,000,000 Mw.

 23. A system as in claim 12, wherein the calcium aluminate particulates are present in the particulate blend at from 40 wt% to 95 wt%.

10 24. A system as in claim 12, wherein the calcium aluminate particulates have an average particulate size from 10 microns to 80 microns, and wherein the polymeric binder particulates have an average particulate size from 0.5 microns to 80 microns.

15 25. A system as in claim 12, wherein the polyol of the liquid vehicle is glycerol.

 26. A system as in claim 12, wherein the polyol of the liquid vehicle is ethoxylated glycerol.

 27. A system as in claim 12, wherein the polyol of the liquid vehicle is polyethylene glycol having a weight average molecular weight from 200 Mw to 2000 Mw.

25 28. A system as in claim 12, wherein the liquid vehicle further includes a colorant.

 29. A system as in claim 12, wherein the liquid vehicle further includes a shrinkage minimizing agent.

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30. A system as in claim 29, wherein the shrinkage minimizing agent is a member selected from the group consisting of 2,5-dimethylpropanediol, pentaerythriol, and combinations thereof.

5 31. A system as in claim 12, wherein the liquid vehicle further comprises a low molecular weight polymer having a weight average molecular weight from 200 Mw to 2000 Mw.

10 32. A system as in claim 12, wherein the liquid vehicle is pH balanced to from 6.5 to 10.0.

15 33. A system as in claim 13, wherein the liquid vehicle includes components configured for improving jettability of the liquid vehicle, said components including water, lower saturated aliphatic alcohols, and surfactants.

20 34. A solid three-dimensional prototype composition, comprising multiple layers of cement deposited in contact with one another, each of said multiple layers of cement comprising a particulate blend including calcium aluminate particulates and polymeric binder particulates, said particulate blend being hydrated and hardened by use of an aqueous polyol-containing liquid vehicle.

 35. A composition as in claim 34, wherein said aqueous polyol-containing liquid vehicle is ink-jetable.

25 36. A composition as in claim 34, wherein said multiple layers of cement includes a lithium ion source.

30 37. A composition as in claim 34, wherein the lithium ion source is selected from the group consisting of lithium hydroxide, lithium citrate, lithium carbonate, lithium formate, and combinations thereof.

38. A composition as in claim 34, wherein the polymeric binder is a member selected from the group consisting of 75% to 100% hydrolyzed polyvinyl alcohol powder, polyacrylamide powder, poly(acrylic acid), poly(acrylamide-co-acrylic acid), poly(vinyl alcohol-co-ethylene), poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid), poly(vinyl pyrrolidone),
5 poly(methylmethacrylate-co-methacrylic acid), soluble starch, methylcellulose, and combinations thereof.

39. A composition as in claim 34, wherein the polyol is selected from the
10 group consisting of glycerol, ethoxylated glycerol, from 200 Mw to 1000 Mw polyethylene glycol, and combinations thereof.

40. A composition as in claim 34, wherein the composition is void of pores larger than about 10 microns.
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41. A composition as in claim 34, wherein upon drying, the composition substantially retains its size and form.
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EPO STYLE CLAIMS AND ABSTRACT

CLAIMS

1. A method for solid free-form fabrication of a three-dimensional object, comprising:
 - a) depositing a particulate blend in a defined region, said particulate blend including calcium aluminate particulates and polymeric binder particulates;
 - b) ink-jetting an aqueous polyol-containing liquid vehicle onto a predetermined area of the particulate blend to form hydrated cement in the predetermined area;
 - c) hardening the hydrated cement; and
 - d) repeating steps a) through c) such that multiple layers of the cement are formed that are bound to one another, thereby forming the three dimensional object.
2. A method as in claim 1, further comprising the step of removing a portion of the particulate blend that does not form the hydrated cement.
3. A method as in claim 1, wherein the polymeric binder particulates are selected from the group consisting of 75% to 100% hydrolyzed polyvinyl alcohol powder, polyacrylamide powder, poly(acrylic acid), poly(acrylamide-co-acrylic acid), poly(vinyl alcohol-co-ethylene), poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid), poly(vinyl pyrrolidone), poly(methylmethacrylate-co-methacrylic acid), soluble starch, methylcellulose, and combinations thereof.
4. A method as in claim 1, wherein the polyol of the liquid vehicle is selected from the group consisting of glycerol, ethoxylated glycerol, polyethylene glycol having a weight average molecular weight from 200 Mw to 2000 Mw, and combinations thereof.
5. A method as in claim 1, wherein the step of hardening is accelerated

by including a particulate lithium ion source in the particulate blend or the liquid vehicle.

6. A method as in claim 1, wherein the liquid vehicle further includes a colorant.

7. A system for solid free-form fabrication of three-dimensional objects, comprising:

a particulate blend of calcium aluminate particulates and polymeric binder particulates; and

an ink-jetable aqueous polyol-containing liquid vehicle configured for hydrating the particulate blend to form a cement.

8. A system as in claim 7, further comprising a lithium ion source admixed as a particulate with the particulate blend, or solvated or suspended in the liquid vehicle.

9. A system as in claim 7, further comprising an ink-jet pen configured for ink-jetting the liquid vehicle onto the particulate blend.

10. A system as in claim 9, further comprising a substrate configured for carrying the particulate blend in a defined region, said defined region being configured with respect to the ink-jet pen such that the liquid vehicle, upon being ink-jetted from the ink-jet pen, contacts the particulate blend.

11. A system as in claim 7, configured for applying multiple layers of cement such that each layer is bound to at least one adjacent layer.

12. A system as in claim 7, wherein the liquid vehicle further includes a shrinkage minimizing agent.

13. A solid three-dimensional prototype composition, comprising multiple

layers of cement deposited in contact with one another, each of said multiple layers of cement comprising a particulate blend including calcium aluminate particulates and polymeric binder particulates, said particulate blend being hydrated and hardened by use of an ink-jettable aqueous polyol-containing liquid vehicle.

14. A composition as in claim 13, wherein said multiple layers of cement includes a lithium ion source.

15. A composition as in claim 13, wherein the polymeric binder is a member selected from the group consisting of 75% to 100% hydrolyzed polyvinyl alcohol powder, polyacrylamide powder, poly(acrylic acid), poly(acrylamide-co-acrylic acid), poly(vinyl alcohol-co-ethylene), poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid), poly(vinyl pyrrolidone), poly(methylmethacrylate-co-methacrylic acid), soluble starch, methylcellulose, and combinations thereof.

16. A composition as in claim 13, wherein the composition is void of pores larger than about 10 microns.

17. A composition as in claim 13, wherein upon drying, the composition substantially retains its size and form.